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THE CALCIUM CARBID METHOD FOR DETERMINING MOISTURE.

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HISTORICAL NOTE.

Calcium carbide was used as a dehydrating agent in obtaining absolute alcohol as early as 1897, by P. Yvon.¹ H. A. Danne in 1900 described before the Society of Chemical Industry of Victoria a method for determining moisture by heating the substance under examination, passing the water vapor through calcium carbide, and measuring the gas obtained. P. V. Dupré used a similar method in the study of ammonium oxalate² and cordite,³ and Cripps and Brown⁴ applied it to spices. Roberts and Fraser⁵ used calcium carbide to determine water in an emulsion of crude petroleum by adding the carbide directly to the emulsion and measuring the gas given off. Irvine Masson⁶ heated calcium carbide in direct contact with a number of substances in a study of the effect on water of crystallization.⁷ Recently Rivett⁸ has used the same method for moisture in butter, allowing the acetylene to escape and estimating its amount by loss in weight of the apparatus.

APPARATUS AND METHOD.

The hope that calcium carbide heated with the material to be analyzed might in some instances afford a more satisfactory means of determining the water present than those now available, led to the following investigation. After a number of pieces of apparatus had been set up and tested, the arrangement shown in figure 1 was adopted and is now in use. As there shown *A* is the generating flask of about 25 cc capacity into which the material to be analyzed is weighed; *B* is the carbide tube with a projection on one side for

¹ Compt. rend., 1897, 125: 1181.

² Analyst, 1905, 80: 266.

³ Analyst, 1906, 81: 213.

⁴ Analyst, 1909, 84: 519.

⁵ J. Soc. Chem. Ind., 1910, 29: 197.

⁶ J. Chem. Soc., 1910, 97: 851.

⁷ See also Chem. News, 1911, 103: 37.

⁸ Chem. News, 1911, 104: 261.

holding 5 cc or more of the carbid; *C* is a 100 cc burette drawn out at the ends to facilitate connections, and is jacketed and the jacket connected with the tap at *D* for the purpose of rapid cooling

and accurate control of temperature; *E* is the leveling vessel. The liquid used in *C* and *E* is mercury or a concentrated solution of sodium chlorid in water, which has stood in contact with acetylene until saturated, and is tinted by means of phenolphthalein and a little sodium hydroxid to facilitate reading.

To operate, introduce a weighed amount of the sample into *A*. If this is not in powder form it is advisable to add barium sulphate, silica, or similar substance and fine sand and mix until the whole is a dry powder, so that the carbid can be brought easily into contact with all parts of the original material, or, the sample may be dissolved or suspended in a suitable liquid and treated with the carbid in this form. Charge tube *B* by filling the side projection with the carbid which has been ground

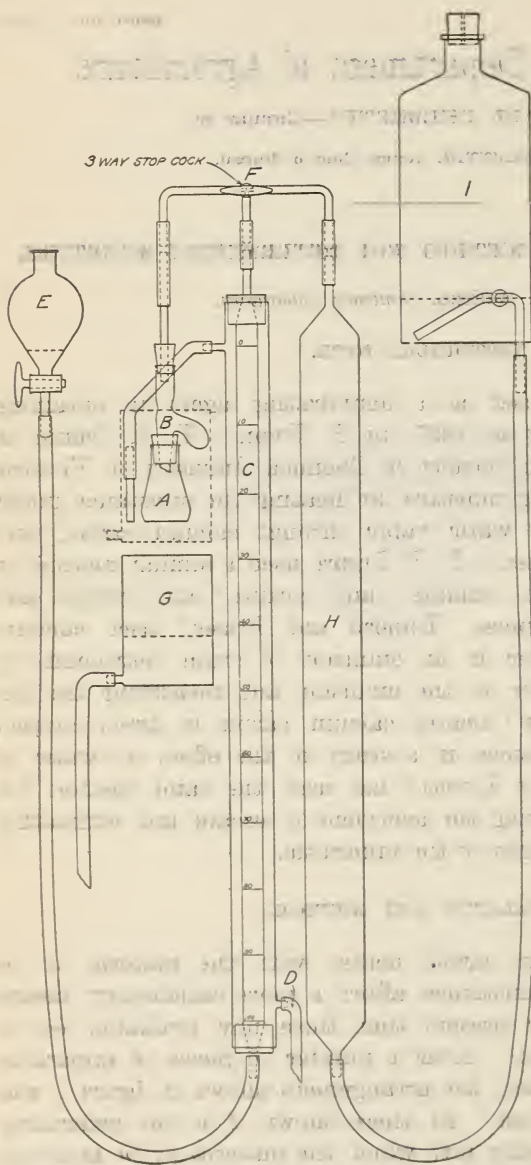


FIG. 1.—Apparatus for the determination of moisture by the calcium carbide method.

in a ball mill to a fine powder. Push a plug of cotton down the vertical part of the tube to the constriction above the projection and place a little carbid above the cotton, holding it in place by another small plug of

cotton, and alternate until the tube is loosely filled with carbid and cotton, thus preventing the escape of any moisture volatilized by the heat of reaction, which is great. Then connect *B* with *C* and *A* with *B* by means of snugly-fitting rubber stoppers and rubber tubing as shown in the cut, no other support being necessary. Open the three-way stopcock *F* to the air by pulling it partly out, and bring the vessel *G* up around *A* so that *A* can be entirely surrounded by water. Allow tap water to run through the jacket about *C* and into *G*, where its height may be maintained as desired by drawing off at the outflow near the bottom of *G*. When the apparatus has cooled to the temperature of the tap water bring the liquid in tube *C* to the zero mark by raising or lowering *E*, turn *F* so as to allow *A* and *B* to communicate with *C*. Lower *G* and introduce a small amount of carbid into *A* by tipping *B* to one side. The rate of reaction is controlled by the rate of admission of the carbid. Keep the level of the water in tube *C* and bulb *E* as nearly the same as possible, by lowering *E* as necessary. When all of the carbid has been added and thoroughly mixed by shaking and rotating the bulb *A*, an easy operation because of the flexible nature of the connection, place a vessel of water in the position formerly occupied by *G*, bring this water to a boil and maintain as long as gas continues to be generated, usually not more than 10 or 15 minutes. In some experiments a glycerin bath has been used, and heated in a few cases as high as 130° C.

When the reaction is over remove the water bath, replace the vessel *G*, and when the apparatus is of the same temperature as in the beginning read off the volume and reduce to standard conditions. Read the temperature of the tap water as recorded by a thermometer suspended in vessel *G*. Ice water was used in some experiments, but the condensation of moisture on the outside of the jacket was objectionable and its use was abandoned. The tube *H* in the apparatus here shown is an auxiliary container, holding about 1,000 cc, for use when the material under examination contains a high per cent of moisture or is of such a nature that a fair sample can not be obtained in gram amounts. In such cases turn the stopcock *F* so as to connect both *C* and *H* with *A*, and at the end of the reaction lead the gas from *H* into *C* in suitable portions, cool, measure, and force out of the apparatus. This is easily done by manipulation of *F* and the leveling vessels *E* and *I*, and is greatly facilitated if before beginning the experiment a permanent support for *E* is so placed that the liquid in *C* stands at the 100 cc mark, and a similar support is arranged for *I* so that the liquid in *H* stands at the zero mark. In order to calculate results it is necessary to know how much gas a known amount of water will yield. This should be determined as nearly as possible under the conditions of the moisture determinations.

According to Lunge¹ 100 grams of calcium carbide yield 40.574 grams (35.019 liters) of acetylene. By this relation, if Moisson's formula ($\text{CaC}_2 + 2\text{H}_2\text{O} = \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$) holds, 1 gram of water should give 623.17 cc of acetylene at standard conditions. In practice about 580 cc are usually obtained.

One series run in a mercury-filled apparatus yielded 607 cc of acetylene for a set of closely checking results. The first series with the apparatus here described measured over a concentrated sodium chloride solution that stood in contact with acetylene until saturated with it gave 586 cc, and the latest determinations gave 582 cc. Little difference in results has been noted whether the carbide was added directly to the water in flask A, in which case the reaction is too vigorous at first, or whether sand, barium sulphate, or cotton was first mixed with the water. Precipitated silica gave low results, indicating that it held about 0.8 per cent of its own weight of water, but more determinations must be made to confirm this. The reaction was complete at 100° C. in all blanks. Heating to 130° C. has no deleterious effect on the rubber connections, but much above that will injure them and ruin the determination. At these temperatures there was no evidence that the acetylene affected the rubber in any way. A good procedure in many cases is to run a determination and follow with a similar amount of material plus a weighed amount of water. Until the action of calcium carbide on all of the materials present and under different conditions is known the necessity of running the blanks in exactly the same way as the determination can not be too strongly emphasized. The value for 1 gram of water being found, the percentage of water in the sample is calculated from the result of the determination.

APPLICATION OF THE METHOD TO DETERMINATIONS OF MOISTURE IN PAINTS AND SOAPS.

The determination of moisture in paint and paint material and soaps being constantly before the Contracts Laboratory, the application of the carbide method to these substances was investigated. Dry pigment could be mixed readily with the carbide and presented no difficulty in operation. (1) White lead is not attacked by calcium carbide, and this method gives good results for hygroscopic moisture, the water of composition not being affected. (2) Gypsum did not react until the temperature neared 100° C.; then the reaction ran rapidly, but not quite all of the two molecules of water was removed. Heating to 135° C. gave the same result as at 100° C. (3) Kaolin yielded by the carbide method the same amount of moisture as is indicated by the loss shown on heating to 100–105° C. The water lost

¹ Chemisch-Technische Untersuchungs Methoden, Aufl. 5, 1905, 2: 710.

at higher temperatures is not affected by calcium carbid. In general, calcium carbid reacts very vigorously with water, but is not reactive in other ways.

Paints or pastes and soaps were mixed with freshly ignited barium sulphate in sufficient quantities to overcome all pastiness; then sand was added to make the mass granular and easily miscible with carbid. After this was accomplished they presented no further operative difficulties. Paints require a large amount of inert material to bring them into good working condition. Rubbing up firm soaps is a tedious operation, while moist soaps lose perceptible amounts of water in the process; hence suspension in liquid was attempted instead. Several liquids were examined to determine their suitability for this purpose, and the effect, if any, of calcium carbid upon them. Liquids likely to be found in paints or soaps were also subjected to experimental tests.

(1) Gasoline vaporized by the heat of reaction and was not condensed at the temperatures used, usually about 5°C . In other words, gasoline has a large and unknown vapor tension at the temperatures used, and its presence or that of similar volatile oils will prevent the use of this method of determining moisture. A plan for absorbing acetylene and thus separating it from these and similar impurities is being considered.

(2) Kerosene inhibited the reaction and considerable shaking was required to keep it from being unduly prolonged. The vapor pressure was found to be low enough to allow its use as a solvent. Cylinder oil and similar mineral lubricating oils run well and are good liquids to use in determining the moisture in substances dissolved or suspended in them.

(3) Toluene is not acted upon by calcium carbid, and its vapor tension is not sufficient to prevent its use as a solvent of suitable materials. It mixes well with paint vehicles and gives more satisfactory results than any other liquid tried, but the boiling point is rather low, and it vaporizes, condensing, however, on cooling. A rather dry sample of soap was not dissolved readily, and hence the action was too much prolonged.

(4) Oleic acid reacts slowly with calcium carbid at 100°C ., yielding acetylene and forming a hard cake removed from the flask only with difficulty. Therefore, it is not suitable as a solvent.

(5) Stearic acid is not attacked by calcium carbid and makes a suitable solvent for some purposes.

(6) Linseed oil is not attacked by calcium carbid. In the presence of water it causes much foaming, and the reaction runs slowly, so that it is not suitable as a solvent, but its presence in paint causes no difficulty.

(7) Turpentine is not attacked by calcium carbide, and its vapor tension is low enough to make it a satisfactory solvent, though the action is somewhat slow in its presence.

(8) Alcohol is not attacked by carbide at its boiling point, but has a considerable vapor tension, for which correction must be made, and it dissolves six times its volume of acetylene at 18°C ., which introduces errors not easily overcome. Ordinary alcohol treated with calcium carbide is dehydrated and saturated with acetylene, and this may be used in some cases without introducing errors. Its wide range as a solvent makes it a desirable reagent.

(9) Amyl alcohol is not affected by carbide and has a lower vapor tension and higher boiling point than ethyl alcohol, making it a useful solvent.

(10) Glycerin is attacked by calcium carbide. Gas equivalent to 12 or 14 per cent of water was obtained in excess of hygroscopic moisture known to be present. It can not be used as a solvent, and its presence in any considerable quantity will vitiate the results.

(11) Anilin has no appreciable vapor tension and gives good results on blanks, though the reaction is somewhat prolonged by its presence.

The examination of these liquids shows that with few exceptions their presence will not interfere with a moisture determination by this method, and that some of them are suitable solvents. But experiments with paints and soaps indicate that as a rule more satisfactory results are obtained by mixing the sample with dry, inert material than by solution or suspension in liquids. Soap in fine shavings to which carbide is added yields much of its moisture, but the reaction is completed too slowly even at 130°C . to be of value. Dry, firm samples dissolve incompletely in alcohol and the reaction is slow; moist samples give good solutions and run well. By rubbing up samples with barium sulphate and sand the most concordant results were obtained, but these differed from results given by other methods of moisture determination, carefully carried out by Mr. G. C. Schmidt in this laboratory. For example, in one case this method gave 28.10 per cent, 28.12 per cent, and 28.03 per cent; by evaporating with alcohol (official method), 25.86 per cent and 26.01 per cent; by Fahrion's method (heating in oleic acid), 28.21 per cent; by difference on complete analysis of the soap, 25.77 per cent and 25.88 per cent.

An extensive examination was made of a sample of castile soap to determine the loss in a vacuum desiccator. Three thoroughly-ground samples of about 2 grams each were weighed out and placed in a vacuum desiccator over sulphuric acid and three similar samples were placed in a second desiccator over calcium carbide lumps and

evacuated. These were weighed daily for two weeks and weekly for seven weeks longer, fresh acid and carbid being introduced occasionally. The total losses were as follows:

Total losses obtained by drying castile soap in a vacuum desiccator for varying periods.

Agents.	Per cent loss during—					
	1 day.	1 week.	5 weeks.	6 weeks.	7 weeks.	9 weeks.
Sulphuric acid.....	6.31	11.12	12.23	12.29	12.29	12.24
Calcium carbid.....	6.14	11.15	12.26	12.33	12.36	12.32

¹ Two samples.

By proposed carbid method: 11.30 and 11.38 per cent loss was found.

Results obtained by Schmidt with other methods: By evaporating with alcohol, 12.82, 13.48, and 12.95 per cent; by Fahrion's method, 13.95, 13.92, and 13.76 per cent; by heating in dynamo oil, 13.56, 13.55, and 13.14 per cent.

Soap powder and bath powder merely mixed with calcium carbid ran satisfactorily, giving concordant results usually somewhat lower than the loss by drying at 105° C.

A number of infants' foods composed of more or less lactose were run for moisture. Being dry powders, they were simply mixed with the carbid. Little gas was generated at ordinary temperature, and on boiling the reaction was slow and prolonged, in some cases an hour or more being necessary for its completion. The results by drying in vacuum at 65° C., by drying in vacuum at 100° C., and by the carbid method are given for comparison.

Comparison of results obtained on dry powdered infants' foods by two methods.

No.	Loss in vacuum.		Carbid method.
	At 65° C.	At 100° C.	
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
994	2.5	3.5	2.89 and 2.93
995	6.5	7.65	6.52 and 6.55
996	1.6	2.4	2.16 and 2.17
997	3.2	4.85	4.26 and 4.23

A sample of pure lactose which lost 5.24 per cent on heating three hours at 105° C. gave gas very slowly with carbid. After nearly two hours' boiling an equivalent of only 1.61 per cent of water was obtained.

Determinations upon flour, leather powder, chrome leather powder, vanilla beans, and sawdust have been run satisfactorily and trust-

worthy results obtained, as shown by comparison with the best methods available. The determination of the water content of fruit juices is at present being investigated. It is believed that calcium carbide has possibilities for the determination of the actual moisture present that warrant a further study of its action under varied conditions.

Approved:

JAMES WILSON,

Secretary of Agriculture.

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